(1)

Abstract:

Source: JP9071404A2

PROBLEM TO BE SOLVED: To obtain hydrogen peroxide purified in high purity by bringing hydrogen peroxide into contact with ozone. SOLUTION: Hydrogen peroxide is brought into contact with ozone to purify hydrogen peroxide. A method for introducing highly concentrated high-purity ozone into hydrogen peroxide and stirring is preferable as the method for bringing hydrogen peroxide into contact with ozone. More preferably hydrogen peroxide is brought into contact with an ozone gas by strong stirring. A method for using a highly concentrated aqueous solution of ozone dissolved in extrapure water for diluting an aqueous solution of hydrogen peroxide is preferable. Since ozone dissolved in hydrogen peroxide by these operations is naturally decomposed, it will not exert a bad influence on facilities, etc., in the following treatments. Purification after bringing ozone into contact with hydrogen peroxide is effectively carried out especially by distillation method, an ion exchange resin, a chelate resin, an adsorption resin, a reverse osmosis membrane or an ultrafiltration membrane. High-purity hydrogen peroxide can be obtained by using the combination of the these purification methods.

Claims of JP9071404:

Machine_translation_Claims:

Claim 1 The purification method of the hydrogen peroxide characterized by contacting a hydrogen peroxide in ozone.

Claim 2 The purification method of the hydrogen peroxide according to claim 1 characterized by distilling as after treatment.

Claim 3 The purification method of the hydrogen peroxide according to claim 1 characterized by making any one or more of ion exchange resin, adsorption resin, chelating resin, a reverse osmotic membrane, and the ultrafiltration membrane contact as after treatment.

Description of JP9071404:

Machine_translation Detailed Description of the Invention:

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Industrial Application This invention relates to the purification method of the hydrogen peroxide from which the impurity contained in hydrogen-peroxide liquid is removed. The hydrogen peroxide refined by the high grade using this invention is used especially suitable for washing of semi-conductor substrates, such as a silicon wafer.

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Description of the Prior Art Generally, a hydrogen peroxide performs removal of organic and an inorganic impurity with distillation, ion exchange resin, etc., and purification is performed. Generally organic impurities are removed by distillation or adsorption resin, and inorganic impurities (metal etc.) are removed by ion exchange resin. Moreover, the hydrogen peroxide of a high grade is further obtained by dipping in adsorption resin, ion exchange resin, etc. a hydrogen peroxide with the low impurity content obtained by distillation. Thus, the refined hydrogen peroxide of a high grade is widely used as a basic or acid hydrogen peroxide in washing of a silicon wafer etc., and whenever still higher purification is being required in connection with the densification of the latest integrated circuit.

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Problem(s) to be Solved by the Invention However, it is more difficult to manufacture the hydrogen peroxide of a high grade rather than a demand will be expected with the present purification technique from now on, for example, about organic impurities, the removal is very difficult for it. Although it now is not still clear about the effect of when these impurities remain to a silicon wafer , the purification technique more than before which removes these impurities with high integration of a semi-conductor is demanded.

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Means for Solving the Problem As a result of inquiring wholeheartedly that the above-mentioned problem should be solved, this invention persons find out that it is very effective in a hydrogen peroxide to contact ozone, and came to complete this invention. That is, since oxidative degradation of the organic impurities in hydrogen-peroxide liquid is carried out, they serve as carbon dioxide gas and are emitted into air by contacting ozone to a hydrogen peroxide, it becomes removable the organic impurities in a hydrogen peroxide . Although there is especially no limit in a hydrogen peroxide about the approach of contacting ozone, it is desirable to blow the ozone gas of high concentration and a high grade, and to perform stirring etc. Although there is especially no limit about stirring here, efficient contact in the ozone gas by strong stirring is more desirable. Moreover, the method of using for dilution of hydrogen peroxide solution the high-concentration ozone water dissolved in ultrapure water etc. is also desirable. The ozone which dissolved into the hydrogen peroxide by these actuation does not have a bad influence on a facility etc. by subsequent processing, in order to decompose automatically.

0005 Especially a limit may not be in the hydrogen peroxide solution to which ozone is contacted, and the hydrogen peroxide of the culmination of purification is sufficient, and a hydrogen peroxide with the high high impurity concentration made in manufacture is sufficient. Moreover, although there is especially no limit in the concentration of the hydrogen peroxide at this time, 1 - 70 % of the weight is preferably good. Moreover, the impurity which was not able to be removed by purification by distillation or ion exchange resin becomes removable more efficiently by purification of subsequent distillation, ion exchange resin, etc. by processing by ozone conventionally. For example, first, by oxidation by ozone, the organic impurities which were not usually able to be removed by distillation are emitted into air as carbon dioxide gas, and decrease in number. At this time, oxidation by ozone is inadequate, and the organic impurities which were not disassembled to carbon dioxide gas exist in a hydrogen peroxide as low-molecular fatty acids, such as formic acid and an acetic acid. These low-molecular fatty acids become possible removing easily by purification by distillation or ion exchange resin after that .

0006 Although what is necessary is just the purification method which especially a limit does not have about the purification after contacting this ozone to a hydrogen peroxide, and removes the impurity in a hydrogen peroxide, purification by distillation, ion exchange resin, chelating resin, adsorption resin, the reverse osmotic membrane, and ultrafiltration membrane is especially effective. Moreover, these purification methods can obtain a high grade hydrogen peroxide by combining and using it. For example, the hydrogen peroxide to which ozone was contacted can be first refined by distillation, and dipping by the column method can be performed in the sequence of adsorption resin, an anion exchange resin, cation exchange resin, and a reverse osmotic membrane, or it can become, and the hydrogen peroxide of a high grade can be obtained. If it is this way of combining, and a method of obtaining the hydrogen peroxide of a high grade more about the number of combination, there will be especially no limit.

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Example

10min stirring was performed blowing the ozone gas of 200 mg/l into 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 1 organic impurities (TOC) by 0.8 l/min. It was 29 ppm when the organic high impurity concentration after processing was measured.

0008 10min stirring was performed blowing the ozone gas of 200 mg/l into 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 2 organic impurities (TOC) by 0.8 l/min. When distillation purification of the obtained hydrogen peroxide was carried out, the organic impurities in a purification hydrogen peroxide were 19 ppm.

0009 10min stirring was performed blowing the ozone gas of 200 mg/l into 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example 3 organic impurities (TOC) by 0.8 l/min. It dipped in the column made from Teflon with a bore of 15mm , and a die length of 30cm filled up with Amberlite IR-120B(H mold, ORGANO CORP. make)20ml which is cation exchange resin about the obtained hydrogen peroxide space-velocity SV10hr-1. Subsequently, it dipped and refined space-velocity SV10hr-1 in the column made from Teflon with a bore of 15mm , and a die length of 30cm filled up with Amberlite IRA-400 (GCC acid type, ORGANO CORP. make) 20ml which is an anion exchange resin. The organic impurities in the obtained purification hydrogen peroxide were 16 ppm.

0010 It is distillation purification ****** in 800ml of 31% of the weight of hydrogen peroxides which contain 50 ppm as example of comparison 1 organic impurities (TOC). The organic impurities in the obtained hydrogen peroxide were 44 ppm.

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Effect of the Invention According to this invention, an impurity can be removed at high effectiveness and adsorption resin, ion exchange resin, etc. can remove organic impurities with low purification effectiveness efficiently especially. The hydrogen peroxide of the high grade obtained by this invention can be used suitable for washing of a silicon wafer.

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(54)【発明の名称】　過酸化水素の精製法

(57)【要約】
【構成】過酸化水素をオゾンに接触させて精製を行う。
【効果】イオン交換樹脂等による精製では効率の低い不純物が除去され高純度に精製された過酸化水素を得ることができる。

【特許請求の範囲】
【請求項１】　過酸化水素をオゾンと接触させることを特徴とする過酸化水素の精製法。
【請求項２】　後処理として、蒸留することを特徴とする請求項１記載の過酸化水素の精製法。
【請求項３】　後処理として、イオン交換樹脂、吸着樹脂、キレート樹脂、逆浸透膜、限外沪過膜のいずれか一つ以上に接触させることを特徴とする請求項１記載の過酸化水素の精製法。
【発明の詳細な説明】
【０００１】
【産業上の利用分野】本発明は過酸化水素液中に含有する不純物を除去する過酸化水素の精製法に関する。本発明を用いて高純度に精製された過酸化水素は、特にシリコンウエハ等の半導体基板の洗浄に好適に用いられる。
【０００２】
【従来の技術】一般に過酸化水素は蒸留法やイオン交換樹脂等によって有機及び無機不純物の除去を行い精製が行われている。一般的には蒸留法または吸着樹脂等によって有機不純物が除去され、イオン交換樹脂によって無機不純物（金属等）が除去されている。また、蒸留法によって得られた不純物含量の低い過酸化水素を吸着樹脂やイオン交換樹脂等に通液することによって、更に高純度の過酸化水素が得られている。このようにして精製された高純度の過酸化水素はシリコンウエハ等の洗浄において塩基性もしくは酸性の過酸化水素として広く使用されており、最近の集積回路の高密度化に伴い、さらに高い精製度が要求されつつある。
【０００３】
【発明が解決しようとする問題点】しかし、現状の精製技術では今後要求が予想されるより高純度の過酸化水素を製造するのは難しく、例えば有機不純物についてはその除去が極めて困難である。これらの不純物がシリコンウエハに残留した場合の影響については現在のところまだ明確ではないが、半導体の高集積化に伴いこれらの不純物を除去する従来以上の精製技術が要望されている。
【０００４】
【問題を解決するための手段】本発明者らは上記の問題を解決すべく鋭意検討した結果、過酸化水素にオゾンを接触させることが極めて有効であることを見いだし本発明を完成するに至った。即ちオゾンを過酸化水素と接触させることによって過酸化水素液中の有機不純物が酸化分解され炭酸ガスとなって空気中に放出されるため、過酸化水素中の有機不純物の除去が可能となる。過酸化水素にオゾンを接触させる方法に関しては特に制限はないが、高濃度、高純度のオゾンガスを吹き込み撹拌等を行うのが好ましい。ここで撹拌に関しては特に制限はないが、強撹拌によるオゾンガスとの効率的接触がより好ましい。また、超純水等に溶解させた高濃度のオゾン水を過酸化水素水の希釈に用いる方法も好ましい。これらの操作で過酸化水素中に溶解したオゾンは自然に分解してしまうため、その後の処理で設備等に悪影響を及ぼすことはない。
【０００５】オゾンを接触させる過酸化水素水には特に制限はなく、精製の最終段階の過酸化水素でも良く、また製造で出来た不純物濃度の高い過酸化水素でも良い。また、このときの過酸化水素の濃度に特に制限はないが好ましくは１～７０重量％が良い。また、従来、蒸留法やイオン交換樹脂による精製で除去出来なかった不純物が、オゾンによって処理することによって、その後の蒸留法やイオン交換樹脂等の精製でより効率的に除去が可能となる。例えば、通常蒸留法で除去出来なかった有機不純物は、まずオゾンによる酸化で炭酸ガスとして空気中に放出され減少する。この時オゾンによる酸化が不十分で炭酸ガスへと分解されなかった有機不純物は蟻酸、酢酸等の低分子脂肪酸として過酸化水素中に存在する。これらの低分子脂肪酸はその後蒸留法やイオン交換樹脂による精製によって容易に除去することが可能となる。
【０００６】このオゾンを過酸化水素に接触させた後の精製に関しては特に制限はなく過酸化水素中の不純物を除去する精製法であれば良いが、特に蒸留法、イオン交換樹脂、キレート樹脂、吸着樹脂、逆浸透膜、限外沪過膜による精製が効果的である。また、これらの精製法は組み合わせて使用することによってより高純度な過酸化水素を得ることができる。例えば、オゾンを接触させた過酸化水素をまず蒸留法で精製し、吸着樹脂、アニオン交換樹脂、カチオン交換樹脂、逆浸透膜の順序でカラム法による通液を行うとかなり高純度の過酸化水素を得る事が出来る。この組み合わせ方、組み合わせの数に関してはより高純度の過酸化水素を得る方法であれば特に制限はない。
【０００７】
【実施例】
実施例１
有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに２００ｍｇ／ｌのオゾンガスを０．８ｌ／ｍｉｎで吹き込みながら１０ｍｉｎ撹拌を行った。処理後の有機不純物濃度を測定したところ２９ｐｐｍであった。
【０００８】実施例２
有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに２００ｍｇ／ｌのオゾンガスを０．８ｌ／ｍｉｎで吹き込みながら１０ｍｉｎ撹拌を行った。得られた過酸化水素を蒸留精製したところ、精製過酸化水素中の有機不純物は１９ｐｐｍであった。
【０００９】実施例３
有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌに２００ｍｇ／ｌのオゾンガスを０．８ｌ／ｍｉｎで吹き込みながら１０ｍｉｎ撹拌を行った。得られた過酸化水素をカチオン交換樹脂であ

るアンバーライトＩＲ－１２０Ｂ（Ｈ型、オルガノ（株）製）２０ｍｌを充填した内径１５ｍｍ、長さ３０ｃｍのテフロン製カラムに空間速度ＳＶ１０ｈｒ$^{-1}$に通液した。次いで、アニオン交換樹脂であるアンバーライトＩＲＡ－４００（重炭酸型、オルガノ（株）製）２０ｍｌを充填した内径１５ｍｍ、長さ３０ｃｍのテフロン製カラムに空間速度ＳＶ１０ｈｒ$^{-1}$に通液し、精製した。得られた精製過酸化水素中の有機不純物は、１６ｐｐｍであった。

【００１０】比較例１

有機不純物（ＴＯＣ）として５０ｐｐｍを含む３１重量％の過酸化水素８００ｍｌを蒸留精製行った。得られた過酸化水素中の有機不純物は４４ｐｐｍであった。

【００１１】

【発明の効果】本発明によれば、不純物を高い効率で除去することができ、特に吸着樹脂、イオン交換樹脂等で精製効率の低い有機不純物を効率よく除去することができる。本発明により得られた高純度の過酸化水素はシリコンウエハの洗浄に好適に使用し得るものである。